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EPR Spectroscopy and Dynamical Behavior of Copper(II) Complexes with N-(Thio)phosphorylated Thioamides

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Abstract

On the basis of EPR and electronic absorption spectra, the type of symmetry and degree of covalence of metal-ligand bonds were determined for copper(II) complexes with N-diisopropoxyphosphorylthiobenzamide (Cu(L1)2, N-diisopropoxythiophosphorylthiobenzamide (Cu(L2)2), N,N'-bis(dusopropoxythiophosphorylamidothiocarbonyl)-1,7-diaza-15-crown-5 (Cu2(L3)2), and N,N'-bis(diisopropoxythiophosphorylamidothiocarbonyl)-1,10-diaza-18-crown-6 (Cu2(L4)2) in liquid and frozen solutions in benzene and carbon tetrachloride. The Cu(L1)2 complex has a planar structure. Cu(L2)2 is represented by two isomers, the planar and tetrahedrally distorted isomers (symmetry D2d). The Cu2(L3)2 and Cu2(L4)2 complexes have D2d symmetry. The tetrahedral distortion was found to enhance with an increase in the sizes of the ligand substituants. An increase in the g‖ and g0 parameters and a decrease in the A‖ and A0 parameters with increasing temperature were shown to be caused by (1) vibronic anharmonicity with mixing of the excited states in the B1g(3dx2-y2) ground state due to the normal vibrations of the B1g and A2u type (in the complexes of the D4h symmetry), or (2) in the B1 (3dx2-y2) ground state due to one B1 normal vibration and two E vibrations in the compounds of the D2d symmetry. The abnormally low values of the A‖ and A0 parameters in the known copper(II) complexes of the D2d symmetry are rationalized by the vibronic mixing of the 4s(a1) orbital in the B2(3dxy) ground state due to the two B2 normal vibrations. The absence of the observed additional hyperfine coupling due to the phosphorus atoms is assigned to the predominant localization of the ligand charge on the sulfur atom of the CS group. However, for the Cu(L2)2 complex, the charge migration between the lig CS and PS groups within the six-membered chelate rings is identified and kinetically characterized.